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(54) Polypropylene resin and procedure for its manufacture

(57) A polypropylene resin is made available that has the following physical properties: (1) a flowability (MFR) of 0.1-1000 g/10 min, measured at 230°C under a load of 2.16 kg; (2) a xylene solubility (CXS) at 23°C of 0.5-5.0 wt.-%; (3) an endothermic main peak temperature (T_{mp}) of 153-163°C, as determined on a melting curve measured with a differential scanning calorimeter (DSC); (4) an eluted amount at a temperature below 80°C of 0.01-3.0 wt.-%, measured with a cross-fractionation chromatograph (CFC); and (5) an isotactic Pentad fraction (mmmm) of 92.0-98.0 wt.-%, measured using ¹³C-NMR.

A procedure for the manufacture of the polypropylene resin mentioned above is also made available that comprises the step of polymerizing propylene in the presence of a catalyst, which comprises the combination of the following components (A), (B) and (C):
Component (A): a solid catalyst, manufactured by reacting a component (A1), which is a solid that contains titanium, magnesium and a halogen as essential components, with a component (A2), which is a silicon compound represented by the general formula $R^1R^{2-3-m}Si(OR^3)_m$ (in which R^1 is a branched aliphatic hydrocarbon group, or a cyclic aliphatic hydrocarbon group; R^2 a hydrocarbon group that....

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Description

The present invention concerns a propylene resin in general terms. The invention concerns in particular a propylene resin of low crystallinity that has specific physical properties and is outstanding in terms of transparency, flexibility and impact resistance.

To date crystalline polypropylene has been industrially produced and in view of its characteristics - such as high crystallinity and high stereo-regularity - has been used in different areas, for instance motor vehicles and electrical household goods. In contrast, amorphous polyethylenes, i.e. atactic polypropylenes, are normally discarded as secondary products for which there is no use. However, in recent years such amorphous polypropylenes have been used in some areas, for instance in adhesives. In addition, in comparison with highly crystalline polypropylenes, polypropylenes of low crystallinity - which are intermediate products between the crystalline polypropylenes above and the amorphous polypropylenes - are for instance polypropylenes of low endothermal main peak temperature (T_{mp}) and low isotactic Pentad fractions (mmmm) that exhibit outstanding flexibility, transparency and impact resistance. In view of these characteristics, such polypropylenes of low crystallinity find uses that differ from those of highly crystalline polypropylenes. That is to say, such polypropylenes of low crystallinity are used in the manufacture of films, sheets, etc. and are used in injection molding, extrusion, etc. Traditional polypropylene resins of low crystallinity contain a mixture of an amorphous polypropylene resin or a polypropylene resin of very low crystallinity and a relatively highly crystalline polypropylene resin. When such resins are molded into films, the amorphous polypropylene readily tends to bleed out of the film, making its surface sticky. In addition, the highly crystalline polypropylene component can lead to molded articles of insufficient flexibility and transparency. It was thus difficult to obtain a polypropylene resin of low crystallinity that has a sufficiently high level of flexibility and transparency and leads to non-tacky molded articles.

It was hence one task of the present invention to eliminate the problems mentioned above and to make available a polypropylene resin of low crystallinity with increased flexibility, transparency and impact resistance and one that can produce non-tacky molded articles.

The inventors of the present invention found that the task mentioned could be accomplished by a polypropylene resin that exhibits a combination of special physical properties

Thus the present invention makes available a polypropylene resin that has the following physical properties:

- (1) a flexibility (MFR) of 0.1-1000 g/10 min, measured at 230°C under a load of 2.16 kg;

- (2) a xylene solubility at 23°C (CXS) of 0.5-5.0 wt.-%;
- (3) an endothermal main peak temperature (T_{mp}) of 153-163°C, as determined on a melting curve measured with a differential scanning calorimeter (DSC);
- (4) an eluted amount at a temperature < 80°C of 0.01-3.0 wt.-%, measured with a cross-fractionation chromatograph (CFC); and
- (5) an isotactic Pentad fraction (mmmm) of 92.0-98.0 wt.-% measured using ¹³C-NMR.

The present invention also makes available a procedure for the manufacture of polypropylene resin mentioned above that comprises the step of polymerization of propylene in the presence of a catalyst that contains the combination of the following components (A), (B) and (C):

Component (A): a solid catalyst obtained by the interaction of a component (A1), which is a solid that contains titanium, magnesium and a halogen as essential constituents, with a component (A2), which is a silicon compound represented by the general formula $R^1R^{2_{3-m}}Si(OR^3)_m$ (in which R^1 is a branched aliphatic hydrocarbon group, or a cyclic aliphatic hydrocarbon group; R^2 a hydrocarbon group that is the same as or different from R^1 , or a hydrocarbon group that contains a hetero-atom; R^3 is a hydrocarbon group with 2 or more C atoms, and $1 \leq m \leq 3$);

Component (B): is an organo-aluminum compound;

Component (C): a silicon compound represented by the general formula $R^4_{4-n}Si(OR^5)_n$ (in which R^4 is a hydrocarbon group, R^5 is a hydrocarbon group with 2 or more C atoms and $1 \leq n \leq 4$).

Detailed description of the invention

Polypropylene resin

The polypropylene of the present invention is characterized by the following physical properties:

The flowability MFR is in the range of 0.1-1000 g/10 min, preferably of 0.1-100 g/10 min, even more preferred of 0.5-50 g/10 min.

If the MFR falls below this range, the formability of the polypropylene resin to a sheet or similar is bad; when the flowability MFR exceeds the range above, the strength of a product – such as a sheet – deteriorates.

The xylene solubility (CXS) at 23°C lies in the range of 0.5-5 wt.-%, preferably of 1.0-4.0 wt.-%. When it exceeds 5 wt.-% the sheet obtained tends to be tacky and if it is of < 0.5 wt.-%, the formability to a sheet is bad.

The endothermal main peak temperature (T_{mp}) on a melting curve obtained by means of a differential scanning calorimeter (DSC) lies in the range of 153-163°C. If the peak temperature is > 163°C, the crystallinity is too high to obtain the desired polypropylene of low crystallinity and if the peak temperature is < 153°C, the xylene solubility (CXS) becomes too high. The endothermal main peak temperature preferably lies in the range of 157-161°C.

The cross-fractionation chromatograph (CFC) can be used to verify the crystallinity distribution of a polymer. Using o-dichloro-benzene as solvent, the amount eluted at a temperature < 80°C is in the range of 0.1-3.0 wt.-%, preferably of 0.1-2.5 wt.-%.

The eluate at a temperature < 80°C corresponds to so-called amorphous atactic polypropylene. If the amount eluted is too large, the sheet formed will be tacky.

The isotactic Pentad fraction (mmmm) measured using ¹³C-NMR lies in the range of 92.0-98.0%, preferably of 92.5-97.0%, even more preferred, of 93.0-96.5%.

When the fraction is too high, the crystallinity is too high to obtain the desired polypropylene resin of low crystallinity; when the fraction is too low, it is again not possible to obtain the desired polypropylene resin of low crystallinity, and this because of the presence of atactic polypropylene. The polypropylene resin of low crystallinity according to the present invention is thus characterized by the low eluted amount at a temperature < 80°C in CFC, even though it is of lower crystallinity than traditionally known propylene resins.

Manufacture

There is no particular limitation in the procedure for the manufacture of the polypropylene resin of low crystallinity in accordance with the present invention. However, it is preferably manufactured by the procedure described below.

Thus the polypropylene resin of low crystallinity according to the invention is preferably manufactured by polymerization of propylene using a catalyst that contains a combination of the following components (A), (B) and (C). If desired, the catalyst may also contain another component, i.e. a fourth component, in addition to the components (A), (B) and (C).

Component (A): a solid catalyst obtained by the interaction of a component (A1), which is a solid that contains titanium, magnesium and a halogen as essential constituents, with a component (A2), which is a silicon compound represented by the general formula $R^1R^2_{3-m}Si(OR^3)_m$ (in which R^1 is a branched aliphatic hydrocarbon group, or a cyclic aliphatic hydrocarbon group; R^2 a hydrocarbon group that is the same as or different from R^1 , or a hydrocarbon group that contains a hetero-atom; R^3 is a hydrocarbon group with 2 or more C atoms, and $1 \leq m \leq 3$);

Component (B): an organo-aluminum compound;

Component (C): a silicon compound represented by the general formula $R^4R^5_nSi(OR^5)_n$ (in which R^4 is a hydrocarbon group, R^5 is a hydrocarbon group with 2 or more C atoms and $1 \leq m \leq 4$).

(1) Solid catalyst component

The component (A) of the catalyst of the present invention is a product obtained by reaction of a specific solid component (component (A1)) with a specific silicon compound (component (A2)). If desired, the component (A) of the present invention may contain also other constituents, in addition to the three essential components above.

Component (A1)

The solid component of the present invention is a solid component for the stereo-specific polymerization of propylene which has titanium, magnesium and halogen as essential constituents. If desired, the solid component may also contain other elements, besides the three essential elements. The elements contained in the solid component may be present in the form of a compound. The elements may furthermore be bonded to each other.

Solid components that contain titanium, magnesium and halogen are *per se* known, for instance from Japanese patent disclosures No. 53-45688, 54-3894, 54-31092, 54-39483, 54-94591, 54-118484, 54-131589, 55-75411, 55-90510, 55-90511, 55-127405, 55-147507, 55-155003, 56-18609, 56-70005, 56-72001, 56-86905, 56-90807, 56-155206, 57-3803, 57-34103, 57-92007, 57-121003, 58-5309, 58-5310, 58-5311, 58-8706, 58-27732, 58-32604, 58-32605, 58-67703, 58-117206, 58-127708, 58-183708, 58-183709, 59-149905, 59-149906 and 63-108008. Any of these known solid components can be used in the present invention.

Magnesium compounds that can serve as magnesium source can include the following: magnesium dihalide, dialkoxy-magnesium, alkoxy-magnesium halide, magnesium-oxyhalide, dialkyl-magnesium, magnesium oxide, magnesium hydroxide, carboxylic acid salts of magnesium, etc. The magnesium compounds

are preferably those prepared with $\text{Mg}(\text{OR}^6)_{2-p}\text{X}_p$ (in which R^6 is a hydrocarbon group with a carbon number preferably of 1-10; X is a halogen, and $0 \leq p \leq 2$), for instance magnesium dihalide and dialkoxy-magnesium.

Titanium compound that can serve as titanium source can be those represented by the general formula $\text{Ti}(\text{OR}^7)_{4-q}\text{X}_q$, where R^7 is a hydrocarbon group with a carbon number of preferably 1-10; X is a halogen and $0 \leq q \leq 4$. The titanium compounds can especially include the following: TiCl_4 , TiBr_4 , $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{O-i-C}_3\text{H}_7)\text{Cl}_3$, $\text{Ti}(\text{O-n-C}_4\text{H}_9)\text{Cl}_3$, $\text{Ti}(\text{O-n-C}_4\text{H}_9)_2\text{Cl}_2$, $\text{Ti}(\text{O-C}_2\text{H}_5)\text{Br}_3$, $\text{Ti}(\text{OC}_2\text{H}_5)(\text{O-n-C}_4\text{H}_9)_2\text{Cl}$, $\text{Ti}(\text{O-n-C}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_6\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{O-i-C}_4\text{H}_9)_2\text{Cl}_2$, $\text{Ti}(\text{O-n-C}_5\text{H}_{11})\text{Cl}_3$, $\text{Ti}(\text{O-n-C}_6\text{H}_{13})\text{Cl}_3$, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{O-n-C}_3\text{H}_7)_4$, $\text{Ti}(\text{O-n-C}_4\text{H}_9)_4$, $\text{Ti}(\text{O-i-C}_4\text{H}_9)_4$, $\text{Ti}(\text{O-n-C}_6\text{H}_{13})_4$, $\text{Ti}(\text{O-n-C}_6\text{H}_{17})_4$ and $\text{Ti}(\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_4$.

In addition, a molecular compound obtained by reacting TiX'_4 (in which X' is halogen) with an electron donor as described subsequently can be used as titanium source. Such molecular compounds can especially comprise the following: $\text{TiCl}_4 \cdot \text{CH}_3\text{COC}_2\text{H}_5$, $\text{TiCl}_4 \cdot \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, $\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{NO}_2$, $\text{TiCl}_4 \cdot \text{CH}_3\text{COCl}$, $\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{COCl}$, $\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$, $\text{TiCl}_4 \cdot \text{ClCOC}_2\text{H}_5$, $\text{TiCl}_4 \cdot \text{C}_4\text{H}_9\text{O}$, etc.

In addition, titanium compounds such as TiCl_3 (that can be obtained by reduction of TiCl_4 with hydrogen, with aluminum metal, or with an organo-metallic compound), TiBr_3 , $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_2$, TiCl_2 , dicyclopentadienyl-titanium dichloride, and cyclopentadienyl-titanium trichloride. Of these titanium compounds TiCl_4 , $\text{Ti}(\text{O-n-C}_4\text{H}_9)_4$ and $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$ are preferred.

In general halogen from the above halogen compounds of magnesium and/or titanium is supplied. Alternatively it can be supplied from other halogen sources, for instance from well-known halogenation reagents that include halogen compounds of aluminum, for instance AlCl_3 , halogen compounds of silicon, for instance SiCl_4 , halogen compounds of phosphorus, such as PCl_3 and PCl_5 , halogen compounds of tungsten, for instance WCl_6 , and halogen compounds of molybdenum, for instance, MoCl_5 . The halogen contained in the catalyst component can be chosen from the groups composed of F, Cl, Br, I or mixtures of these. Chlorine is especially preferred.

The solid component for use in the present invention may contain other constituents, in addition to the essential components, for instance aluminum components, such as $\text{Al}(\text{OC}_2\text{H}_5)_3$, $\text{Al}(\text{O-i-C}_3\text{H}_7)_3$ and $\text{Al}(\text{OCH}_3)_2\text{Cl}$, and boron compounds, such as $\text{B}(\text{OCH}_3)_3$, $\text{B}(\text{OC}_2\text{H}_5)_3$ and $\text{B}(\text{OC}_6\text{H}_5)_3$. These components may remain in the solid component as aluminum and boron components.

In addition, during the manufacture of the solid component an electron donor may be used as internal donor. The electron donors (internal donors) that can be used in the manufacture of the solid component can include the following:

oxygen-containing electron donors, for instance alcohols, phenols, ketones, aldehydes, carboxylic acids, esters of organic or inorganic acids, ethers, acid amides and acid anhydrides; and nitrogen-containing electron donors, for instance ammonia, amines, nitriles and isocyanates.

The electron donors may especially include: (a) alcohols with 1-18 C atoms, for instance methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, dodecanol, octadecyl alcohol, benzyl alcohol, phenyl-ethyl alcohol and isopropyl-benzyl alcohol; (b) phenols with 6-25 C atoms that may contain alkyl groups, for instance phenol, cresol, xlenol, ethyl-phenol, propyl-phenol, isopropyl-phenol, nonyl-phenol and naphthol groups; (c) ketones with 3-15 C atoms, for instance acetone, methyl-ethyl ketone, methyl-isobutyl ketone, acetone and benzophenone; (d) aldehydes with 2-15 C atoms, for instance acetaldehyde, propionaldehyde, octylaldehyde, benzaldehyde, tolualdehyde and naphthaldehyde; (e) esters of organic acids with 2-20 C atoms: monoesters of organic acids, for instance methyl formate, methyl acetate, ethyl acetate, vinyl acetate, propyl acetate, octyl acetate, cyclohexyl acetate, Cellosolve acetate, ethyl propionate, ethyl butyrate, ethyl valerate, ethyl stearate, methyl chloroacetate, ethyl-dichloro acetate, methyl methacrylate, ethyl crotonate, cyclohexan-methyl carboxylate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl benzoate, cyclohexyl benzoate, phenyl benzoate, benzyl benzoate, Cellosolve benzoate, methyl toluylate, ethyl toluylate, amyl toluylate, ethylethyl benzoate, methyl anisate, ethyl anisate, ethylethoxy benzoate, γ -butyrolactone, α -valerolactone, coumarin and phthalide; and esters of organic polyacids, for instance diethyl phthalate, dibutyl phthalate, diheptyl phthalate, diethyl succinate, dibutyl maleate, 1,2-cyclohexan-diethyl carboxylate, ethylene carbonate, norbornan-dienyl-1,2-dimethyl carboxylate, cyclopropan-1,2-dicarboxylic acid-n-hexyl- and 1,1-cyclobutan-diethyl carboxylate; (f) esters of inorganic acids that include silicic acid esters (except silicon compounds represented by the general formula $R^1R^2R^3Si(OR^3)_m$, above), for instance ethyl silicate, butyl silicate and phenyl-triethoxy silane; (g) acid halides with 2-15 C atoms, for instance acetyl chloride, benzoyl chloride, toluic acid chloride, anisic acid chloride, phthaloyl chloride and isophthaloyl chloride; (h) ethers with 2-20 C atoms, for instance methyl ether, ethyl ether, isopropyl ether, butyl ether, amyl ether, tetrahydrofuran, anisole and diphenyl ether; (i) amides, for instance acid amides, benzoic acid amide and toluic acid amide; (j) amines, for instance methyl amine, ethyl amine, diethyl amine, tributyl amine, piperidine, tribenzyl amine, aniline, pyridine, picoline, and tetramethyl diamine; (k) nitriles, for instance acetonitrile, benzonitrile and phenyl-acetic acid nitrile; (l) alkoxy-ester compounds, for instance 2-(ethoxy-methyl) ethyl benzoate, 2-(tert.-butoxy-methyl)-ethyl benzoate, 3-ethoxy-2-ethylphenyl propionate, 3-ethyl-ethoxy propionate, 3-ethoxy-2-sec.-ethyl-butyl propionate and 3-ethoxy-2-tert.-ethyl-butyl propionate; and (m) ketone-ester compounds, for instance 2-ethyl-benzoyl benzoate, 2-(4'-methyl-benzoyl)-ethyl benzoate and 2-benzoyl-4,5-ethyl-dimethyl benzoate. The electron donors are preferably ester compounds of organic acids and acid halide compounds, more preferred phthalic

acid diester compounds, Cellosolve acetate-ester compounds and phthalic acid dihalides.

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Component (A2)

The silicon compound to be used in the present invention is described by a general formula $R^1R^2_{3-m}Si(OR^3)_m$ (in which R^1 is a branched aliphatic hydrocarbon group, or a cyclic aliphatic hydrocarbon group; R^2 is a hydrocarbon group that is the same as or different from R^1 , or a hydrocarbon group that contains a hetero-atom; R^3 is a hydrocarbon group with 2 or more C atoms, and $1 \leq m \leq 3$). The silicon compound can be a mixture of silicon compounds represented by the general formula shown above. When R^1 is a branched aliphatic hydrocarbon group, then the branched chain is preferably branched from a C atom next to a Si atom. The branched chain is preferably an alkyl group, a cyclo-alkyl group, or an aryl group (for instance a phenyl group or a methyl-substituted phenyl group). R^1 is preferably a group in which the C atom is next to a Si atom, i.e. the C atom in α -position is a secondary or tertiary, especially a tertiary C atom. When R^1 is a branched hydrocarbon group, then the number of C atoms is in general of 3-20, preferably of 4-10. When R^1 is a cyclic hydrocarbon group, the number of C atoms is in general of 4-20, preferably of 5-10. R^2 is a hydrocarbon group that is the same as R^1 or differs from it, or R^2 is a heteroatom-containing hydrocarbon group. The number of C atoms is here in general of 1-20, preferably of 1-10. R^3 is a hydrocarbon group that has 2 or more C atoms and is preferably an aliphatic hydrocarbon group with 2-20, preferably 2-10 and even more preferred, 2-4 C atoms.

The silicon compounds to be used in the present invention can especially include those shown on the following pages.

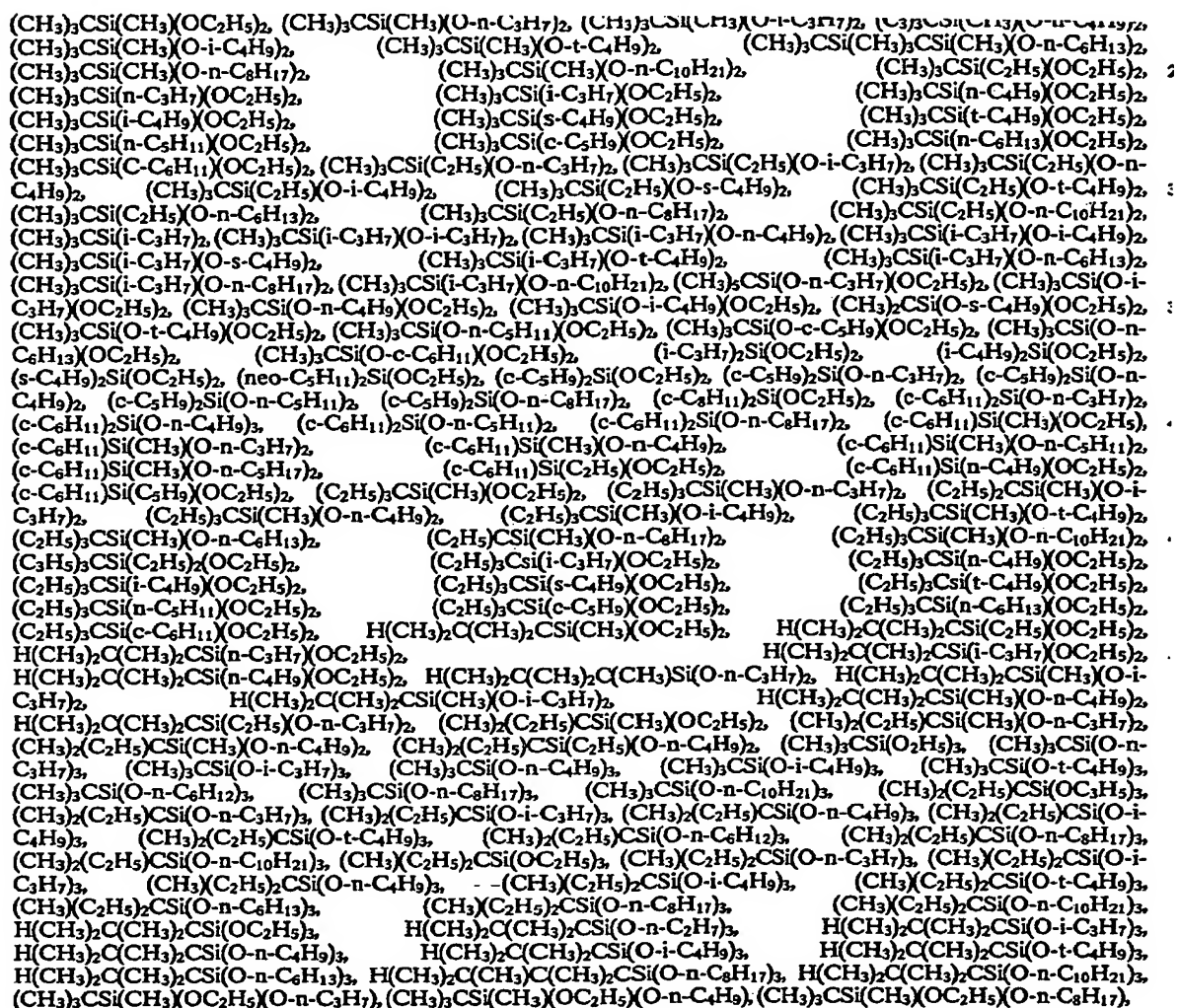
As established there, the component (A) of the present invention can contain – if necessary in addition to the essential components mentioned earlier – also optional components. The following compounds are appropriately used as such optional components.

(A) Vinyl-silane compounds

Vinyl-silane compounds to be used in the present invention may have a structure in which the vinyl group ($CH_2=CH-$) replaces at least on H atom in monosilane (SiH_4) and in which a halogen (preferably Cl), an alkyl group

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(preferably a hydrocarbon group with 1-12 C atoms), an aryl group (preferably phenyl), an alkoxy group (preferably an alkoxy group with 1-12 C atoms) or similar replaces one of the remaining H atoms.





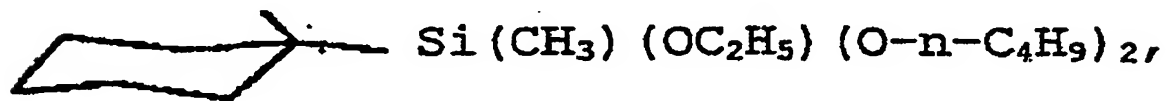
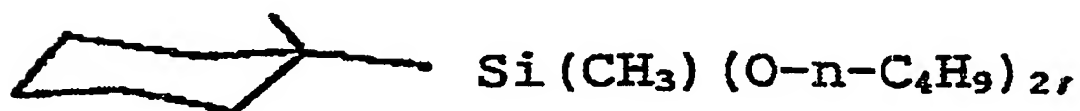
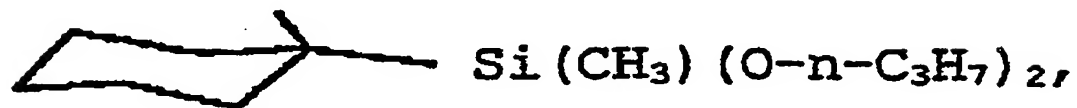
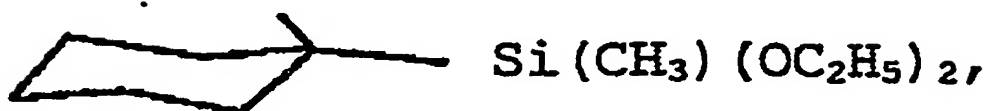
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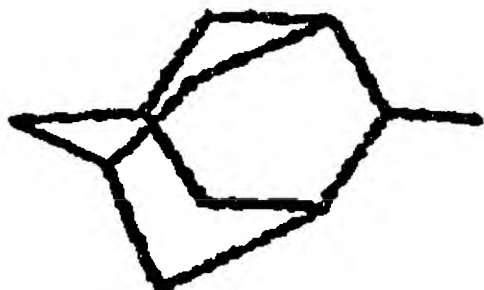


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The vinyl compounds can especially include the following: $\text{CH}_2=\text{CH}-\text{SiH}_3$, $\text{CH}_2=\text{CH}-\text{SiH}_2(\text{CH}_3)$, $\text{CH}_2=\text{CH}-\text{SiH}(\text{CH}_3)_2$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_3$, $\text{CH}_2=\text{SiCl}_3$, $\text{CH}_2=\text{CH}-\text{SiCl}_2(\text{CH}_3)$, $\text{CH}_2=\text{CH}-\text{SiH}(\text{CH}_3)_2$, $\text{CH}_2=\text{CH}-\text{SiH}(\text{Cl})(\text{CH}_3)$, $\text{CH}_2=\text{CH}-\text{Si}(\text{C}_2\text{H}_5)_3$, $\text{CH}_2=\text{CH}-\text{SiCl}(\text{C}_2\text{H}_5)_2$, $\text{CH}_2=\text{CH}-\text{SiCl}_2(\text{C}_2\text{H}_5)$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)_2$, $\text{CH}_2=\text{CH}-\text{Si}(\text{n}-\text{C}_4\text{H}_9)$, $\text{CH}_2=\text{CH}-\text{Si}(\text{C}_6\text{H}_5)_3$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2(\text{C}_6\text{H}_4)(\text{CH}_3)$, $\text{CH}_2=\text{CH}-(\text{CH}_3)_2\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_2(\text{CH}=\text{CH}_2)$, $(\text{CH}_2=\text{CH})_2\text{SiH}_2$, $(\text{CH}_2=\text{CH})_2\text{SiCl}_2$, $(\text{CH}_2=\text{CH})_2\text{Si}(\text{CH}_3)_2$ and $(\text{CH}_2=\text{CH})_2\text{Si}(\text{C}_6\text{H}_5)_2$.

(B) Organo-metallic compounds

It is also possible to use organo-metallic compounds of metals that belong to groups I through III of the periodic system. The organo-metallic compounds to be used in the present invention have at least one organic group-metal bond. Such organic groups are typically hydrocarbon groups in which the number of C atoms is in general of 1-20, preferably of 1-6. At least one valence of the metal of the organo-metallic compound is satisfied with an organic group and the remaining valence (valences) (if there are any) can be satisfied with a H atom, a halogen atom, a hydrocarbyl-oxy* group (the number of C atoms can in general be of 1-20, preferably of 1-6), or be satisfied with another metal in the same organo-metallic compound via oxygen atoms (for instance $-\text{O}-\text{Al}(\text{CH}_3)-$ in the case of methyl alumoxan) or similar.

Such organo-metallic compounds can in particular include the following: (a) organo-lithium compounds, for instance methyl-lithium, n-butyl-lithium and tert.-butyl-lithium; (b) organo-magnesium compounds, for instance butyl-ethyl-magnesium, dibutyl-magnesium, hexyl-ethyl-magnesium, butyl-magnesium chloride and tert.-butyl-magnesium bromide; (c) organo-zinc compounds, such as diethyl-zinc and dibutyl-zinc; and (d) organo-aluminum compounds, for instance trimethyl-aluminum, triethyl-aluminum, tri-isobutyl-aluminum, tri-n-hexyl-aluminum, diethyl-aluminum chloride, diethyl-aluminum halide, diethyl-aluminum

* "Hydrocarbyloxygruppe" in the German original. No English equivalent found [T.N.]

ethoxide, ethyl-aluminum sesqui-chloride, ethyl-aluminum dichloride, methyl-alumoxane. Organo-aluminum compounds are especially preferred.

Each of optional components (A) and (B) mentioned above can be used individually or as a mixture of two or more. The use of the optional components may reinforce the effects of the present invention.

Manufacture of component (A)

The component (A) can be manufactured - in an intermediate step or a final step - by stepwise or simultaneous reaction between the essential and optional components described above and washing the resulting product with an organic solvent, such as a hydrocarbon, or a halogenated hydrocarbon.

Thus component (A) can be manufactured in a two step procedure, where the solid component (A1) that contains titanium, magnesium and a halogen as essential constituents, is manufactured first and the solid product is reacted with the silicon compound (A2); or it can be manufactured in a single step procedure, where the silicon compound (A2) may be present in the procedure for the manufacture of the solid component (A1), to thus manufacture component (A) directly. The procedure mentioned first is the preferred of these procedures.

The conditions for the realization of the reaction between the constituents to form component (A) are not particularly limited, provided the desired effects of the present invention are achieved. However, in general the following conditions are used. The contact temperature is preferably in the range of between -50 to approx. 200°C, preferably between 0 and 100°C. The contact can be achieved using mechanical means, such as a rotating ball mill, a vibration mill, a jet mill or a paddle mill, or occur according to a procedure that includes diluting the components with an inert diluent and stirring the system. The inert diluent can be an aliphatic or aromatic hydrocarbon or a halogenated hydrocarbon, or a polysiloxane.

Even though the amount of each constituent that forms component (A) is not particularly limited, provided the desired effects of the present invention are achieved, the following amounts can in general be used. The molar ratio of the titanium compound to the magnesium compound may lie in the range of 0.0001-1000, preferably of 0.01-10. If a halogen compound is used as halogen source, then the molar ratio of halogen compound to magnesium compound may lie in the range of 0.01-1000, preferably of 0.1-100, regardless of the whether the titanium compound and/or the magnesium compound contain a halogen. The silicon compound, component (A2), can be used in such an amount that the molar ratio of silicon to titanium in the resulting component (A) is in the range of 0.01-1000, preferably of 0.1-100.

When the vinyl-silane compound is used, it can be used in an amount such that the molar ratio of vinyl-silane compound to the titanium component in the resulting component (A) lies in the range of 0.001-1000, preferably of 0.01-

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100. When the aluminum and boron compounds are used, the molar ratios of these compounds to the magnesium compound can lie in the range of 0.001-100, preferably of 0.01-1. When the electron donor is used, the molar ratio of electron donor to the magnesium compound can lie in the range of 0.001-10, preferably of 0.01-5.

Component (A) can be manufactured when components (A1) and (A2) are reacted, if necessary using further components, such as an electron donor, for instance in accordance with the following procedure:

- (a) a procedure in which a magnesium halide is reacted with an electron donor, a titanium-containing compound, a silicon compound and a sulfonate;
- (b) a procedure in which aluminum oxide or magnesium oxide are treated with a phosphorus halide and the treated aluminum oxide or magnesium oxide is reacted with a magnesium halide, an electron donor, a silicon compound, a titanium halide and a sulfonate;
- (c) a procedure in which a magnesium halide is reacted with titanium tetra-alkoxide and a special polymeric silicon compound, the resulting solid component is reacted with a titanium halide and/or a silicon halide, the resulting reaction product is mixed with an inert organic solvent and then the reaction product is further reacted with a silicon compound and a sulfonate, either simultaneously or stepwise. The polymeric silicon compound preferred is one described by the formula $-(\text{SiH}(\text{R}^8)\text{-O})_r$ (where R^8 is a hydrocarbon group with 1-10 C atoms, r representing a degree of polymerization such that the viscosity of the polymeric silicon compound lies in the range of 1-100 centistoke. Specifically preferred examples for the polymeric silicon compound include methyl-hydro-polysiloxane, ethyl-hydro-polysiloxane, phenyl-hydro-polysiloxane, cyclo-hexyl-hydro-polysiloxane, 1,3,5,7-tetramethyl-cyclo-tetrasiloxane and 1,3,5,7,9-pentamethyl-cyclo-pentasiloxane;
- d) a procedure in which a magnesium compound is dissolved in titanium tetra-alkoxide and/or an electron donor, a solid component is precipitated with a halogenation agent or a titanium halide and where this solid component is reacted simultaneously or stepwise with a silicon compound, a titanium compound and a sulfonate.
- e) a procedure in which an organo-magnesium compound, for instance a Grignard reagent, is reacted with a halogenation agent, a reducing agent or similar, where the resulting product is reacted with an electron donor if

necessary, and the then resulting product is reacted simultaneously or stepwise with a silicon compound, a titanium compound and a sulfonate.

f) a procedure in which an alkoxy-magnesium compound is reacted either simultaneously or stepwise with a halogenation agent and/or a titanium compound, a silicon compound and a sulfonate, in the presence or absence of an electron donor, or where they are reacted separately with each other.

The procedures (a), (c), (d) and (f) are preferred among those listed above. Component (A) can be washed either in an intermediate step or as a final step in its manufacture, with an inert organic solvent, for instance an aliphatic or aromatic hydrocarbon (for instance hexane, heptane, toluene or cyclohexane), or a halogenated hydrocarbon (for instance n-butyl chloride, 1,2-dichloro-ethane, carbon tetrachloride or chloro-benzene).

The component (A) to be used in the present invention may also be one that has undergone a prepolymerization procedure, a polymerization of a compound containing a vinyl group, for instance an olefin, a diene compound or styrene, in the presence of the component (A) manufactured above. The olefins to be used in the prepolymerization have 2-20 C atoms, for instance ethylene, propylene, 1-butene, 3-methyl-buten-1, 1-pentene, 1-hexene, 4-methyl-penten-1, 1-octene, 1-decene, 1-undecene and 1-eicosene. Some specific examples of diene compounds can include 1,3-butadiene, isoprene, 1,4-hexadiene, 1,5-hexadiene, 1,3-pentadiene, 1,4-pentadiene, 2,4-pentadiene, 2,6-octadiene, cis-2,trans-4-hexadiene, trans-2,trans-4-hexdiene, 1,3-heptadiene, 1,4-heptadiene, 1,5-heptadiene, 1,6-heptadiene, 2,4-heptadiene, dicyclo-pentadiene, 1,3-cyclo-hexadiene, 1,4-cyclo-hexadiene, cyclopentadiene, 1,3-cyclo-heptadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,9-decadiene, 1,13-tetradecadiene, p-divinyl-benzene, m-divinyl-benzene, o-divinyl-benzene and dicyclo-pentadiene. The styrenes can include styrene, α -methyl-styrene, allyl-benzene and chloro-styrene.

The reaction conditions in the prepolymerization procedures mentioned above are not particularly limited, provided the desired effects of the present invention are achieved; of course the following conditions can be used, in general. The amount of prepolymerized compound that contains a vinyl group can lie in the range of 0.01-100 g, preferably of 0.1-50 g, even more preferred, of 0.5-10 g per 1 g of solid catalyst component. The reaction temperature during prepolymerization can be of -150 to 150°C, preferably of 0-100°C. The reaction temperature of the prepolymerization is preferably lower than that of the "main polymerization" of propylene. In general the reaction is preferably performed with stirring. In this case an inert solvent can be used, for instance n-hexane or n-heptane.

(2) Component of an organo-aluminum compound

The organo-aluminum component (component (B)) to be used in the present invention can be one represented by the general formula $R^9_{3-s}AlX_s$, or $R^{10}_{3-t}Al(OR^{11})_t$ in which R^9 and R^{10} are a hydrocarbon group with 1-20 C atoms or H, R^{11} is a hydrocarbon group, X is a halogen and s and t are $0 \leq s \leq 3$, $0 < t < 3$. Some specific examples include (a) trialkyl-aluminum, for instance trimethyl-aluminum, triethyl-aluminum, tri-isobutyl-aluminum, trihexyl-aluminum, trioctyl-aluminum and tridecyl-aluminum; (b) alkyl-aluminum halides, for instance diethyl-aluminum monochloride, di-isobutyl-aluminum monochloride, ethyl-aluminum sesquichloride and ethyl-aluminum dichloride; (c) alkyl-aluminum hydrides, for instance diethyl-aluminum hydride and di-isobutyl-aluminum hydride; and (d) alkyl-aluminum alkoxides, for instance diethyl-aluminum ethoxide and diethyl-aluminum phenoxide.

These organo-aluminum compounds (a) through (d) can be used in combination. For instance, the combinations triethyl-aluminum/diethyl-aluminum ethoxide, diethyl-aluminum monochloride/diethyl-aluminum ethoxide, ethyl-aluminum dichloride/ethyl-aluminum diethoxide, triethyl-aluminum/diethyl-aluminum ethoxide/diethyl-aluminum monochloride, etc. can be used.

In addition the organic aluminum compounds (a) through (d) can be combined with alumoxans, for instance methyl-alumoxan, ethyl-alumoxan and isobutyl-alumoxan.

(3) Component of silicon compound

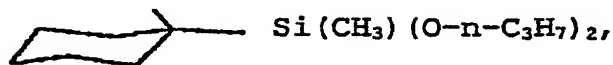
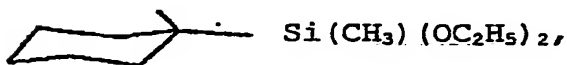
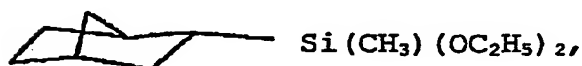
The silicon compound (component (C)) to be used in the present invention is represented by the general formula $R^4_{4-n}Si(OR^5)_n$ (in which R^4 is a hydrocarbon group, R^5 is a hydrocarbon group with 2 or more C atoms and $1 \leq n \leq 4$). The number of C atoms in R^4 in general lies in the range of 1-30, preferably of 1-20; the number of C atoms in R^5 in general lies in the range of 1-30, preferably of 2-20, preferably of 2-10.

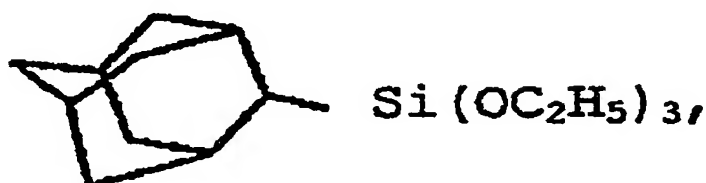
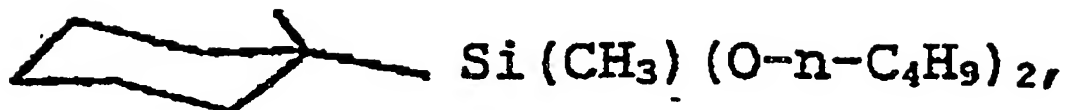
Some specific examples for such silicon compounds include

[illegible]

$(C_2H_5)_3CSi(C_2H_5)(OC_2H_5)_2$, $(C_2H_5)_3CSi(n-C_3H_7)(OC_2H_5)_2$, $(C_2H_5)_3CSi(i-C_3H_7)(OC_2H_5)_2$,
 $(C_2H_5)_3CSi(n-C_4H_9)(OC_2H_5)_2$, $(C_2H_5)_3CSi(i-C_4H_9)(OC_2H_5)_2$, $(C_2H_5)_3CSi(s-C_4H_9)(OC_2H_5)_2$,
 $(C_2H_5)_3CSi(t-C_4H_9)(OC_2H_5)_2$, $(C_2H_5)_3CSi(n-C_5H_{11})(OC_2H_5)_2$, $(C_2H_5)_3CSi(c-C_5H_9)(OC_2H_5)_2$,
 $(C_2H_5)_3CSi(n-C_6H_{13})(OC_2H_5)_2$, $(C_2H_5)_3CSi(c-C_6H_{11})(OC_2H_5)_2$, $H(CH_3)_2C(CH_3)_2CSi(CH_3)(OC_2H_5)_2$,
 $H(CH_3)_2C(CH_3)_2CSi(C_2H_5)(OC_2H_5)_2$, $H(CH_3)_2C(CH_3)_2CSi(n-C_3H_7)(OC_2H_5)_2$, $H(CH_3)_2C(CH_3)_2CSi(i-C_3H_7)(OC_2H_5)_2$,
 $H(CH_3)_2C(CH_3)_2CSi(i-C_3H_7)(OC_2H_5)_2$, $H(CH_3)_2C(CH_3)_2CSi(n-C_4H_9)(OC_2H_5)_2$, $H(CH_3)_2C(CH_3)_2CSi(i-C_4H_9)(OC_2H_5)_2$,
 $C_3H_7)_2$, $H(CH_3)_2C(CH_3)_2CSi(CH_3)(O-i-C_3H_7)_2$, $H(CH_3)_2C(CH_3)_2CSi(CH_3)(O-n-C_4H_9)_2$,
 $H(CH_3)_2C(CH_3)_2CSi(C_2H_5)(O-n-C_3H_7)_2$, $(CH_3)_2(C_2H_5)CSi(CH_3)(OC_2H_5)_2$, $(CH_3)_2(C_2H_5)CSi(CH_3)(O-n-$
 $C_3H_7)_2$, $(CH_3)_2(C_2H_5)CSi(CH_3)(O-n-C_4H_9)_2$, $(CH_3)_3CSi(OC_2H_5)_3$,
 $(CH_3)_3CSi(O-n-C_3H_7)_3$, $(CH_3)_3CSi(O-i-C_3H_7)_3$, $(CH_3)_3CSi(O-n-C_4H_9)_3$, $(CH_3)_3CSi(O-i-C_4H_9)_3$, $(CH_3)_3CSi(O-t-$
 $C_4H_9)_3$, $(CH_3)_3CSi(O-n-C_6H_{12})_3$, $(CH_3)_3CSi(O-n-C_6H_{17})_3$, $(CH_3)_3CSi(O-n-C_{10}H_{21})_3$, $(CH_3)_2(C_2H_5)CSi(OC_2H_5)_3$,

$(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-n-\text{C}_3\text{H}_7)_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-i-\text{C}_3\text{H}_7)_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-n-\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-t-\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-i-\text{C}_6\text{H}_{13})_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-n-\text{C}_5\text{H}_{11})_3$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CSi}(\text{O}-n-\text{C}_{10}\text{H}_{21})_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{OC}_2\text{H}_5)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-n-\text{C}_3\text{H}_7)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{C}_3\text{H}_7)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-n-\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-i-\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-t-\text{C}_4\text{H}_9)_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-n-\text{C}_6\text{H}_{13})_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-n-\text{C}_8\text{H}_{17})_3$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CSi}(\text{O}-n-\text{C}_{10}\text{H}_{21})_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{OC}_2\text{H}_5)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-n-\text{C}_3\text{H}_7)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-i-\text{C}_3\text{H}_7)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-n-\text{C}_4\text{H}_9)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-i-\text{C}_4\text{H}_9)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-t-\text{C}_4\text{H}_9)_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-n-\text{C}_6\text{H}_{13})_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-n-\text{C}_8\text{H}_{17})_3$, $\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CSi}(\text{O}-n-\text{C}_{10}\text{H}_{21})_3$, $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)(\text{O}-n-\text{C}_3\text{H}_7)$, $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)(\text{O}-n-\text{C}_4\text{H}_9)$, $(\text{CH}_3)_3\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)(\text{O}-n-\text{C}_5\text{H}_{11})$





In the polymerization of propylene according to the present invention the amounts of the components (A), (B) and (C) to be used are not particularly limited, provided the advantageous effects of the present invention are achieved. However, in general the following amounts can be used. The molar ratio of component (B) to the titanium compound of component (A) can lie in the range of 0.001-10,000, preferably of 1-1000. The molar ratio of component (C) to component (B) can lie in the range of 0.001-1000, preferably of 0.01-10 and even more preferred, of 0.05-2.

Polymerization of propylene

The polymerization of propylene for the manufacture of polypropylene of low crystallinity according to the present invention can be performed using any polymerization technique, for instance suspension polymerization using a hydrocarbon solvent, or a solvent-free liquid phase polymerization (mass polymerization), solution polymerization, or vapor phase polymerization. In the case of suspension polymerization, aliphatic or aromatic solvents can be used, for instance pentane, hexane, heptane, cyclohexane, benzene and toluene, or mixtures of these. In addition the polymerization can be performed continuously, in batches, in several steps, or one that includes a prepolymerization step. The

polymerization temperature can in general lie in the range of 20-200°C, preferably of 50-150°C. The polymerization pressure can be in the range of atmospheric pressure to approx. 300 kg/cm², preferably between atmospheric pressure and 100 kg/cm². As is known, hydrogen can be used to control the molecular weight, during polymerization.

The Examples below further elucidate the present invention, but do not limit it.

The following procedures and equipment are used to measure the physical properties of the polypropylene obtained in the Examples.

MFR

Equipment: apparatus to measure the melt-flow index manufactured by the Takara Co., Ltd. Measurement procedure according to JIS-K6758.

CXS

Measurement procedure: a sample (approx. 5 g) is weighed precisely and dissolved completely in xylene (300 mL) at 140°C, the solution is then cooled to 23°C and allowed to stand for 12 h. The solution is filtered and the amount of solid dissolved in the filtrate is isolated. The weight ratio of the isolated solid to the sample weight is determined.

Differential scanning calorimeter (DSC)

Equipment: DSC-2, manufactured by Perkin-Elmer Co., Ltd.
Measurement procedure: a sample (approx. 5 g) is melted in 3 minutes at 200°C, then the temperature is reduced to 30°C at a rate of 10 °C/min. The temperature is then increased to 200°C at a rate of 10°C/min. The melting curve was obtained in this manner; the curve was used to determine the endothermal main peak temperature (T_{mp}).

Cross-fractionation chromatograph (CFC)

Equipment: Cross-fractionation chromatograph D150A manufactured by Mitsubishi Chemical Co., Ltd.
Measurement procedure: a sample of the polymer solution (solvent: o-dichlorobenzene) was sent to temperature raise elution fractionation (TREF), where the temperature of the solution was raised from 0°C to 140°C over 24 hours. The elution curve was obtained in this manner and from it, the weight ratio of the polymer fraction eluted at a temperature of < 80°C to total polymer was determined.

¹³C-NMR

Equipment: GSX-270 manufactured by JEOL LTD.

Measurement procedure: The proton decoupling procedure was performed at a measurement temperature of 130°C using o-dichloro-benzene/heavy benzene as solvent, where the weight ratio of the mmmm component to the total polymer was determined.

Example 1

Manufacture of component (A)

200 mL dehydrated and deoxidized n-heptane are placed in a flask sufficiently washed with nitrogen; then 0.4 mol MgCl_2 and 0.8 mol $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)$

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are added to perform the reaction for 2 h at 95°C. At the end of the reaction the temperature was lowered to 40°C. The 48 mL methyl-hydro-polysiloxane (20 centistoke) were added to the flask and the reaction was allowed to proceed for 3 h. The resulting solid was washed with n-heptane.

Next 50 mL n-heptane purified as above are placed in a flask sufficiently purified with nitrogen; then 0.24 mol on a Mg-atomic basis of the solid synthesized above were added into the flask. Then 0.24 mol SiCl_4 were mixed with 25 mL n-heptane; the mixture was added dropwise at 30°C, over 30 min, to the flask and the mixture was allowed to react for 3 h at 70°C. Once the reaction was completed, the reaction product was washed with n-heptane. Then 1.6 mL $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$ were added to the flask as the silicon compound to react with the reaction product obtained. The resulting product was washed sufficiently with n-heptane, obtaining component (A), containing magnesium chloride as main constituent. The titanium content in component (A) was of 2.3 wt.-%.

Polymerization of polypropylene

500 mL of sufficiently dehydrated and deoxidized n-heptane, 125 mL triethyl-aluminum as component (B), 20.8 mg $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$ as component (C) and 15 mg of the component (A) manufactured above were placed in a stainless steel autoclave with a capacity of 1.5 L, equipped with a stirrer and a thermostat. Then 60 mL hydrogen were introduced into the autoclave and the temperature and pressure of the system were increased to perform the polymerization of propylene under the following conditions: polymerization pressure = 5 kg/cm² G, polymerization temperature = 75°C and polymerization time = 2 h. At the end of polymerization the resulting polymer suspension was filtered to separate the polymer. The polymer was then dried. As

a result 289.5 g polymer were obtained. The filtrate contained 0.48 g polymer. The polymer obtained had a MFR of 4.5 g/10 min, a xylene solubility (CXS) at 23°C of 2.8 wt.-%, a peak temperature (T_{mp}) of 160.1°C on a melting curve obtained by DSC, and an eluted amount at a temperature < 80°C of 0.52 wt.-%, measured by CFC, and an isotactic Pentad fraction (mmmm) of 96.0%, measured by NMR.

Example 2

Manufacture of component (A)

100 mL dehydrated and deoxidized toluene are placed in a flask sufficiently washed with nitrogen; then 20 g Mg(OEt)₂ were added forming a suspension. Then 60 mL TiCl₄ were added into the flask and the temperature of the system was raised from room temperature to 90°C. Then 3.3 mL Cellosolve acetate were added to the flask and the temperature was raised to 100°C; the reaction was allowed to proceed for 3 h. At the end of the reaction the reaction product was washed sufficiently with toluene. Then 100 mL TiCl₄ and 100 mL toluene were added to the flask and the reaction was performed at 110°C for 3 h. At the end of the reaction the reaction product was washed sufficiently with n-heptane.

Next 50 mL n-heptane purified in the same manner as above were placed in a flask sufficiently washed with nitrogen; then 5 g of the solid component synthesized above, 0.5 mL divinyl-dimethyl-silane, 1.1 mL (i-C₃H₇)₂Si(OC₂H₅)₂ and 3.6 g Al(n-C₆H₁₃)₃ were added into the flask, where the reaction was performed at 50°C during 2 h. The resulting product was then sufficiently washed with n-heptane, producing component (A). The titanium content of component (A) was of 2.9 wt.-%.

Polymerization of propylene

The polymerization of propylene was performed as in Example 1 except that the polymerization temperature was changed to 85°C and that 27.0 mL of (CH₃)₃CSi(CH₃)(OC₂H₅)₂ were used as component (C). As a result 301.7 g polymer were obtained. 0.66 g polymer were recovered from the filtrate. The polymer had a MFR of 6.2 g/10 min, a xylene solubility (CXS) at 23°C of 3.7 wt.-%, a peak temperature (T_{mp}) of 157°C on a melting curve obtained by DSC, an amount eluted at < 80°C of 0.67 wt.-% measured by CFC and an isotactic Pentad fraction (mmmm) of 96.0% measured by NMR.

Examples 3 through 5

Using the solid catalyst (component (A)) of Example 1, the same polymerization as in Example 1 was performed, except that silicon compounds as shown in Table 1 were used as component (C).

Comparison example 1

A solid catalyst was manufactured as in Example 1, except that

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$(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$ was not used as component (A2). The polymerization was performed as in Example 1. As a result 168.6 g of polymer were obtained. 1.10 g polymer were recovered from the filtrate. The polymer obtained had a MFR of 7.8 g/10 min, a xylene solubility (CXS) at 23°C of 6.7 wt.-%, a peak temperature (T_{mp}) of 152.5°C on a melting curve obtained by DSC, an amount eluted at < 180°C of 3.5 wt.-% measured by CFC and an isotactic Pentad fraction (mmmm) of 92.0% measured by NMR.

Comparison example 2

Using the solid catalyst (component (A)) of Example 1, the same polymerization as in that Example was performed, except that component (C) $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$ was not used. As a result 234.6 g polymer were obtained. 1.20 g polymer were recovered from the filtrate. The polymer obtained had a MFR of 6.6 g/10 min, a xylene solubility (CXS) at 23°C of 5.5 wt.-%, a peak temperature (T_{mp}) of 154.8°C on a melting curve obtained by DSC, an amount eluted at < 180°C of 3.5 wt.-% measured by CFC and an isotactic Pentad fraction (mmmm) of 93.0% measured by NMR.

Comparison example 3

150 mL dehydrated and deoxidized n-heptane were placed in a flask sufficiently washed with nitrogen and then 60 mL TiCl_4 were added into the flask. Separately, 120 mL n-heptane and 9.5 g diethyl-aluminum chloride were placed in a dropping funnel. The flask was cooled to -10°C; diethyl-aluminum chloride was added dropwise from the dropping funnel to the content of the flask, over a period of 3 h. The reaction was allowed to continue for another hour at -10°C. The temperature of the system was then increased to 65°C over 1 h and the reaction was allowed to proceed for another hour. At the end of the reaction the reaction product was washed sufficiently with n-heptane; a solid titanium chloride composition was obtained.

Next a mixed solution of 250 mL n-heptane and 100 mL di-isoamyl ether were added to titanium chloride composition obtained above, to perform a 1 h long reaction at 35°C. At the end of the reaction, the reaction product was

sufficiently washed with n-heptane. Then a mixed solution of 250 mL n-heptane and 120 mL TiCl_4 was allowed to react during 2 h at 65°C with the above reaction product. At the end of the reaction the reaction product was sufficiently washed with n-heptane; a solid catalyst component was obtained.

Polymerization of propylene

500 mL of sufficiently dehydrated and deoxidizes n-heptane, 500 mg diethyl-aluminum chloride and 50 mg of the solid catalyst were placed in a stainless steel autoclave with a capacity of 1.5 L, equipped with a stirrer and a thermostat. Then 350 mL hydrogen were introduced into the autoclave and the system temperature and pressure were increased to perform the polymerization of propylene under the following conditions: polymerization pressure = 5 kg/cm^2 G, polymerization temperature = 65°C and polymerization time = 2 h. At the end of polymerization, the resulting polymer suspension was filtered to separate the polymer; the polymer was then dried. As a result, 79.7 g polymer were obtained. 2.8 g polymer were recovered from the filtrate. The polymer obtained had an MFR of 8.1 g/10 min, a xylene solubility (CXS) at 23°C of 3.4 wt.-%, a peak temperature (T_{mp}) of 159.8°C on a melting curve obtained by DSC, an amount eluted at $< 80^\circ\text{C}$ of 5.1 wt.-% measured by CFC and an isotactic Pentad fraction (mmmm) of 91.5% measured by NMR.

The results from the above Examples and Comparison examples are listed in Table 1.

Table 1

Bei- spiel Nr.	Komponente (A1) (Menge)	Komponente (C) (Menge)	Polymer- ausbeute	MFR	CXS	Tmp	Eluierte Menge (CFC, unter 80°C)	η _{inh}
			g	g/10 min g/10 min	Gew.-% Gew.-%	°C	Gew.-%	
Bsp. 1	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(1.6ml)} \end{array}$	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(20.8mg)} \end{array}$	289,5	4,5	2,8	160,1	0,62	96,0
Bsp. 2	$\begin{array}{c} \text{i-Pr} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{i-Pr} \quad \text{OEt} \\ \text{(1.1ml)} \end{array}$	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(27.0mg)} \end{array}$	301,7	6,2	3,7	157,3	0,67	96,0
Bsp. 3	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(1.6ml)} \end{array}$	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{n-Pr} \quad \text{OEt} \\ \text{(37.1mg)} \end{array}$	283,4	4,1	3,2	157,6	0,64	95,0
Bsp. 4	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(1.6ml)} \end{array}$	$\begin{array}{c} \text{c-C}_6\text{H}_5 \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{c-C}_6\text{H}_5 \quad \text{OEt} \\ \text{(26.8mg)} \end{array}$	255,7	4,3	3,0	158,6	0,61	95,0
Bsp. 5	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(1.6ml)} \end{array}$	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{n-C}_6\text{H}_{13} \quad \text{OEt} \\ \text{(29.2mg)} \end{array}$	243,8	5,8	3,2	158,0	0,71	95,0
Vgl.- Bsp. 1	—	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(20.8mg)} \end{array}$	168,6	7,8	6,7	152,5	3,5	92,0
Vgl.- Bsp. 2	$\begin{array}{c} \text{t-Bu} \quad \text{OEt} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OEt} \\ \text{(1.6ml)} \end{array}$		234,6	6,6	5,5	154,8	3,5	93,0
Vgl.- Bsp. 3	—		79,7	8,1	3,4	159,8	5,1	91,5

[KEY: Beispiel Nr. = Example No. Komponente (Menge) = Component (amount)
 ausbeute = polymer yield Eluierte Menge unter 80°C = amount eluted below 80°C Bsp =
 Example Vgl.-Bsp = comparison example]

Patent claims

1. Polypropylene resin with the following physical properties:
 - (1) a flowability (MFR) of 0.1-1000 g/10 min, measured at 230°C under a load of 2.16 kg;
 - (2) a xylene solubility (CXS) at 23°C of 0.5-5.0 wt.-%;
 - (3) an endothermal main peak temperature (T_{mp}) of 153-163°C as determined on a melting curve obtained with a differential scanning calorimeter (DSC);
 - (4) an amount eluted at < 80°C of 0.01-3.0 wt.-%, measured with a cross-fractionation chromatograph (CFC); and

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- (5) an isotactic Pentad fraction (mmmm) of 92.0-98.0 wt.-%, measured by ¹³C-NMR.
2. Procedure for the manufacture of a polypropylene resin according to claim 1 that comprises the step of polymerization of propylene in the presence of a catalyst that contains a combination of the components (A), (B) and (C) as follows:

Component (A): a solid catalyst obtained by reaction of a component (A1) which is solid and contains titanium, magnesium and halogen as essential constituents, with a component (A2) of a silicon compound, represented by the general formula $R^1R^{2-3-m}Si(OR^3)_m$ (in which R^1 is a branched aliphatic hydrocarbon group, or a cyclic aliphatic hydrocarbon group; R^2 a hydrocarbon group that is either the same as or different from R^1 , or a hydrocarbon group that contains a hetero-atom; R^3 is a hydrocarbon group with two or more C atoms and $1 \leq m \leq 3$);

Component (B): an organo-aluminum compound;

Component (C): a silicon compound represented by the general formula $R^4R^{5-4-n}Si(OR^5)_n$ (where R^4 is a hydrocarbon group, R^5 a hydrocarbon group with 2 or more C atoms and $1 \leq n \leq 4$).